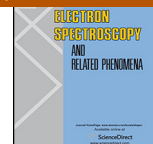


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Related Phenomenajournal homepage: www.elsevier.com/locate/elspecValence photodissociation of trifluoroethyl iodide investigated by
photoelectron photoion coincidence spectroscopyA.F. Lago^{*}, B.C. da Silva, P.J. Arakaki

Centro de Ciências Naturais e Humanas, Universidade Federal do ABC (UFABC), 09210-170 Santo André, SP, Brazil

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ABSTRACT

Dissociative photoionization of trifluoroethyl iodide ($\text{C}_2\text{H}_2\text{F}_3\text{I}$) molecule has been investigated by electron-ion coincidence technique (PEPICO) and VUV synchrotron radiation. Mass spectra have been recorded for this molecule in the photon energy range of 10–22 eV. The molecular ion as well as cationic fragments have been detected and analyzed as a function of photon energy and the main dissociation pathways are proposed. We also performed *ab initio* calculations for the neutral molecule, its cation and the ion fragments in order to determine electronic and structural parameters.

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1. Introduction

The interest in the study of the photoionization of halogenated molecules has increased notably in the last decade. It is in part due to the importance of these molecules in atmospheric chemistry, since many compounds of this class have been observed in the troposphere, and consequently been considered important sources of reactive halogens in atmosphere. In this sense, experimental and theoretical photoionization approaches [1] are known as powerful tools to understand electronic structures, photon induced molecular reaction dynamics, identify atomic, molecular and radical photodissociation products and derive their energetics and reactivity. In particular, photoionization experiments involving the detection of ions in coincidence with electrons are of great importance for the study of ion dissociation dynamics as well as for the determination of accurate ion thermochemistry [1–4].

In the present work we report the first photodissociation studies for the trifluoroethyl iodide molecule, following valence level photoionization, by using photoelectron photoion coincidence (PEPICO) [5] and synchrotron radiation [6]. Quantum chemical calculations based on *ab initio* methods have also been performed for this molecule, in order to obtain additional information on the geometry parameters electronic structures and energetics.

The trifluoroethyl iodide molecule, $\text{C}_2\text{H}_2\text{F}_3\text{I}$ (also named 1,1,1-trifluoro-2-iodoethane), is an important alkyl halide compound

used in the organic chemistry industry [7–9]. Despite its relevance, not many spectroscopic studies have been reported for this molecule in the literature [10,11]. However, several studies on the photoionization of other iodine containing molecules may be found [12–17]. The adiabatic ionization energy of $\text{C}_2\text{H}_2\text{F}_3\text{I}$ molecule has been reported as 10.00 ± 0.01 eV [18]. The 70 eV electron impact mass spectrum of $\text{C}_2\text{H}_2\text{F}_3\text{I}$ is reported by NIST [19].

2. Experimental approach

A Wiley–McLaren type time-of-flight mass spectrometer [20,21] was employed for mass/charge analysis of the ionic species. Our photoelectron photoion coincidence (PEPICO) set-up, procedures and data treatment have been previously described [22,23]. Briefly, a continuous 766 V/cm DC electric field is applied to the first ion acceleration stage. The electrons and positively charged ions, produced following the interaction of the VUV light beam with the sample, are accelerated in opposite directions and detected by pairs of micro-channel plate (MCP) detectors mounted in chevron configuration and coupled to 50 Ohm adapted anodes. Electrons detected without energy analysis and the cations give rise, respectively, to start and stop signals to the time to digital converter (TDC), which allows simultaneous multihit capability within 1 ns resolution. These signals are correlated and expressed as mass/charge ratio \times intensity, resulting in a mass spectrum (PEPICO). The time-of-flight spectrometer was designed to avoid angular discrimination of the ejected ions with kinetic energy release up to 40 eV. Methods of subtraction of fortuitous coincidences in the PEPICO spectra are described in the literature [5].

^{*} Corresponding author. Tel.: +55 11 4996 8377.

E-mail addresses: alexandre.lago@ufabc.edu.br, aleflago@gmail.com (A.F. Lago).

However, in the present work, given the very good signal to noise ratio in our experiments and the absence of multiple ionization in this energy range, the contribution of fortuitous coincidences to the spectra is very small.

The experiments were performed at the Brazilian Synchrotron Light Laboratory (LNLS) located at Campinas, Brazil. Vacuum ultra-violet (VUV) photons in the range from 10 to 22 eV emitted from the toroidal grating monochromator (TGM) beamline [24] were used in the present studies. This beamline currently operates in the 7.3–330 eV range, provides a photon flux (ph/s/mm²) of 7×10^{10} at 100 mA at 35 eV and spot size of $2 \text{ mm} \times 500 \mu\text{m}$. The energy resolution ($E/\Delta E$) is about 500–700 in the 10–22 eV range.

The measurements have been undertaken using a gas harmonics filter coupled to the TGM beamline at LNLS, which has been described in detail elsewhere [25]. This noble gas harmonic filter (effective cut-off energy at 21.54 eV, for Neon) is based on a very efficient differential pumping system, and provides an efficient depletion of high order harmonics in the VUV (which is of paramount importance for photoionization and fragmentation studies in this energy range). By using adequate noble gases this filter we are also able to obtain a precise photon energy calibration of the beamline, as well as a means for determining the energy resolution.

The present electron ion coincidence experiments have been performed with the TOF drift tube axis and the extraction fields oriented parallel relative to the plane of polarization of the synchrotron light. The sample was commercially obtained from Sigma–Aldrich with purity of 99%. No further purification was used except for degassing the liquid samples by multiple freeze–pump–thaw cycles before admitting the vapor into the chamber. A base pressure of about 1×10^{-8} Torr was maintained in the vacuum chamber, and the experiments were performed with the sample in the low 10^{-7} Torr range.

3. Theoretical methods

The quantum chemical computations were carried out using the Gaussian 09 package [26]. General calculation procedures and theoretical methods are described in the literature [27–29]. We have performed ab initio calculations using Moller–Plesset perturbation theory and density functional theory (DFT) for the trifluoroethyl iodide molecule, its molecular cation and the most important ionic fragments.

The molecular and fragment ions structures have been optimized at B3LYP MP2 and MP4(SDQ) levels of theory, together with the 6–311++G(3df,2pd) basis set, except for the heavy iodine containing species which, instead, were treated using the effective core potential (ECP) LANL2DZ [30,31]. We extracted the electronic structure information and structural parameters from the final optimized structures. We have also performed calculations using Outer Valence Green's Function (OVGF) approximation [32] in order to estimate the valence ionization energies.

4. Results and discussion

The $\text{C}_2\text{H}_2\text{F}_3\text{I}$ molecule belongs to the C_s symmetry group, and the optimized geometry for this neutral molecule in its ground state, which results from our calculations at the MP4(SDQ)/LanL2DZ level of theory, is depicted in Fig. 1. The optimized geometry of the molecular cation using the same method is also shown in this Figure. All optimized geometries reported in this work correspond to energy minima, which were also confirmed through vibrational frequency analysis [29]. The optimized structures computed for the main fragment ions from the photodissociation of the $\text{C}_2\text{H}_2\text{F}_3\text{I}$ molecule are shown in Fig. 2.

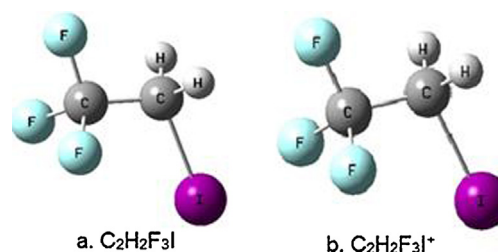


Fig. 1. Optimized molecular structures of $\text{C}_2\text{H}_2\text{F}_3\text{I}$ and $\text{C}_2\text{H}_2\text{F}_3\text{I}^+$ computed at the MP4(SDQ)/LanL2DZ level of theory.

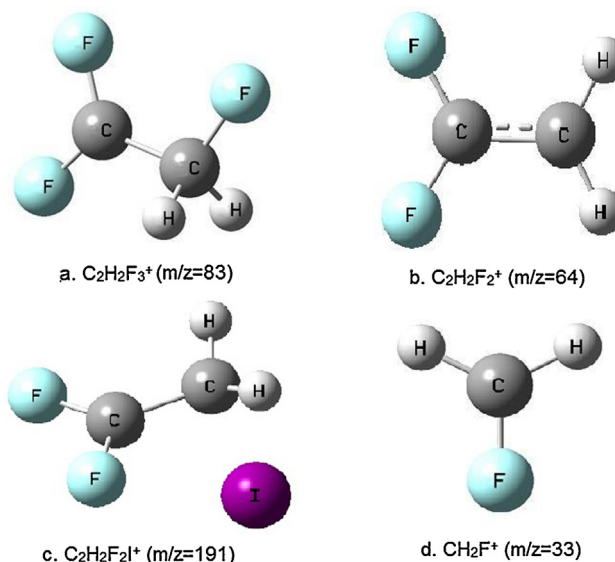


Fig. 2. Optimized structures of trifluoroethyl iodide fragment ions. Fragments a, b and d were computed at the MP2/6–311++G(3df,2pd) level of theory, and fragment c was computed at the MP4(SDQ)/LanL2DZ level.

The main structural parameters of $\text{C}_2\text{H}_2\text{F}_3\text{I}$ and its first cation are presented in Table 1. In general, we note some differences in the geometries of these species. The carbon–fluorine bond is seen shortened while the carbon–iodine bond is stretched as we move from neutral to cation. In addition, we also note important modifications in the bonding angles. Despite our general understanding of valence molecular orbitals as being highly delocalized, these results provide an important evidence of the electron density distortion due to the perturbation caused by the valence electron ionization, which may subsequently lead to the molecular dissociations, as observed in our experiments.

Table 1

Selected geometrical parameters of trifluoroethyl iodide molecule and molecular cation computed at MP4(SDQ)/LanL2DZ level of theory. R represents bond distances (in angstroms) and A represents the angles.

Parameters	$\text{C}_2\text{H}_2\text{F}_3\text{I}$	$\text{C}_2\text{H}_2\text{F}_3\text{I}^+$
R (C ₁ –C ₂)	1.530	1.545
R (C ₁ –F ₅)	1.422	1.397
R (C ₁ –F ₆)	1.413	1.409
R (C ₂ –H ₃)	1.100	1.103
R (C ₂ –I ₈)	2.193	2.217
A (C ₁ , C ₂ , H ₃)	108.299	111.181
A (C ₁ , C ₂ , I ₈)	114.000	111.117
A (C ₂ , C ₁ , F ₅)	109.929	108.998
A (C ₂ , C ₁ , F ₆)	113.509	111.137
A (H ₃ , C ₂ , H ₄)	111.076	111.616
A (H ₃ , C ₂ , I ₈)	107.599	105.744
A (F ₅ , C ₁ , F ₆)	106.199	108.888
A (F ₆ , C ₁ , F ₇)	106.986	107.738

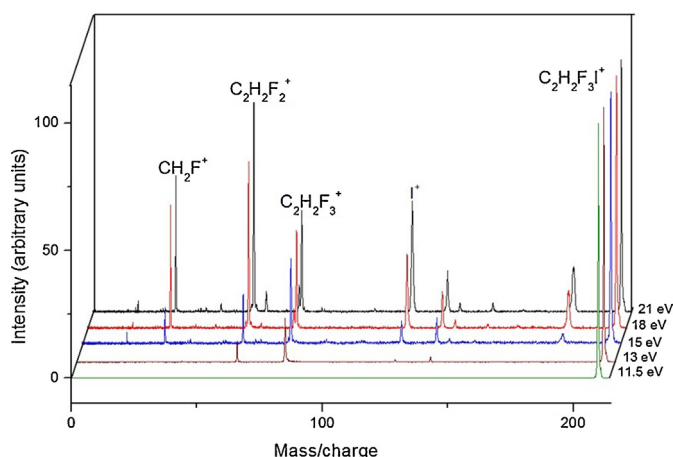
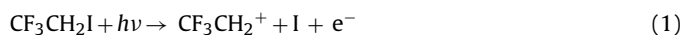


Fig. 3. Photoelectron photoion coincidence (PEPICO) spectra of $C_2H_2F_3I$ molecule in the photon energy range of 10–22 eV.

From the optimized geometries of neutral molecule and its first cation, obtained at MP4(SDQ)/LanL2DZ level of theory, we were also able to compute the first adiabatic ionization energy (IE) for the trifluoroethyl iodide molecule as approximately 9.96 eV, and as 10.04 eV using Outer Valence Green's Function approximation (OVGF/SDD). We estimate an error of about 0.1 eV in our energy calculations. The theoretical IE values are in very good agreement to the reported experimental value of 10.00 eV [18]. In this sense, we believe that our calculated structural parameters for this molecule presented in Table 1 are consistent and reliable.

Electron ion coincidence (PEPICO) spectra of $C_2H_2F_3I$ molecule were recorded in the range from 10 to 21.5 eV photon energy. The PEPICO mass spectra obtained at selected energies are shown in Fig. 3. In general, as expected, as we increase the photon energy in the VUV range, the PEPICO spectra for this molecule feature diverse fragmentation patterns, leading to singly charged species and neutral radicals. We discuss the most important dissociation pathways of trifluoroethyl iodide molecule following VUV photoionization. Considering that the detected photoelectrons are not energy analyzed in the present work, we estimate the accuracy in the determinations of appearance energies in the present work to be better than 0.2 eV, although higher accuracy would be achievable by using threshold electron techniques [3,4].

From Fig. 3 we observe that only the parent ion ($C_2H_2F_3I^+$) is found at energies from 10 eV to near 12 eV. The first dissociation channel of trifluoroethyl iodide molecule occurs at about 12.13 eV and corresponds to the rupture of the long carbon–iodine bond (see Table 1) resulting in the fragment $CF_3CH_2^+$ ($m/z=83$) as in the following reaction (1)



This is a direct fast fragmentation pathway that was also predicted from our calculations, given the enlargement of the C–I bond distance as we ionize the molecule (see Fig. 1).

As for the fragment ion $CF_3CH_2^+$ ($m/z=83$) resulting from reaction (1), we should point out the results from our ab initio calculations which indicate that this molecular structure is much less stable than that for the isomer $CF_2CH_2F^+$ ($m/z=83$) shown in Fig. 2a. We speculate that the former fragment ion $CF_3CH_2^+$ could undergo isomerization reaction [3] with energy barrier into the isomer $CF_2CH_2F^+$, which in turn would favor further fragmentation and recombination reactions [33].

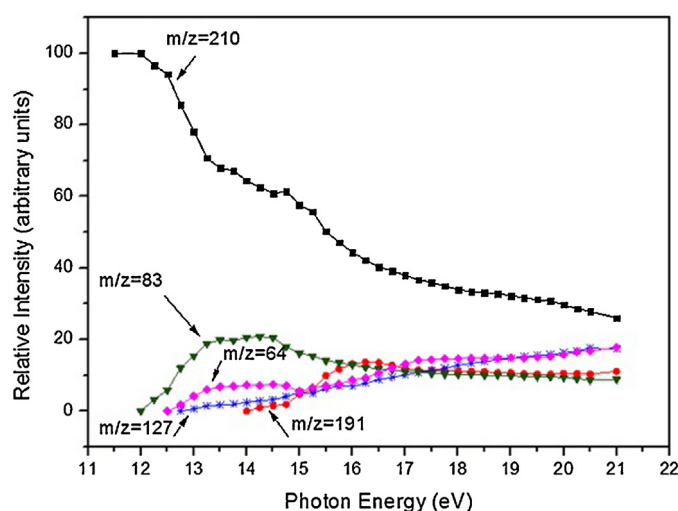
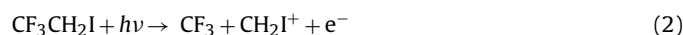


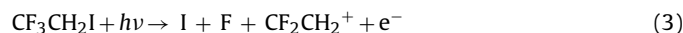
Fig. 4. Breakdown diagram showing the most important ion species in the photon energy range of 10–22 eV.

The following dissociation channel opens up at approximately 12.63 eV, which results from the carbon–carbon breakage and leads to CH_2I^+ ($m/z=141$) fragment ion illustrated in reaction (2):



From Table 1 we also note that the C–C bond distance is increased from the neutral to the cation, and as the internal energy increases we expect it would favor this bonding dissociation.

At about the same energy (12.63 eV) we also observe the formation of the $CF_2CH_2^+$ ($m/z=64$) fragment, which is formed via concerted carbon–iodine and carbon–fluorine bond cleavages (3):



Although the iodine atom has a reported ionization energy of 10.45 eV [34], the atomic iodine fragment cation I^+ ($m/z=127$) from $C_2H_2F_3I$ is first noted in our spectra only at approximately 12.88 eV. This is an indication of the relatively strong bonding of this molecule, and also point out to the preferential tendency of the iodine atom to be released from the molecule as a neutral, as opposed to the more intense $CF_3CH_2^+$ fragment, especially at photon energies below 14 eV. At higher energies the ion I^+ becomes increasingly more important.

A less intense ion fragment $CF_2CH_2I^+$ ($m/z=191$), corresponding to a fluorine atom loss, is observed in the spectra starting from approximately 14.13 eV. It is interesting to note from our results that this fragment is formed at 2.0 ± 0.2 eV higher than the $CF_3CH_2^+$ (iodine loss). It is expected, since the more electronegative fluorine atom forms much stronger bonding as compared to the heavier iodine atom. This may be used as direct measure of the C–F and C–I bond strength differences in the CF_2CH_2I molecule. For sake of comparison, the methane substituted molecules represented by CH_3X have bond dissociation energy (BDE) of 115 kcal/mol for carbon–fluorine and 57.6 kcal/mol for carbon–iodine, which gives a difference of approximately 2.49 eV [35], and also corroborates with our results.

The partial ion yields (PIY) of the most important ionic species associated with the VUV photodissociation of trifluoroethyl iodide molecule are shown in Fig. 4, in the form of a breakdown diagram. The PIY curves clearly show photon energy dependence, pointing out to the contributions of ionizations from molecular orbitals with the different compositions leading to the formation of the observed ionic products either via parallel or via sequential reactions.

Table 2
Selected branching ratios for the $C_2H_2F_3I$ dissociative photoionization products in the VUV range.

<i>m/z</i>	Ion	Ion relative intensities (%) / energy (eV)									
		12.0	13.0	14.0	15.0	16.0	17.0	18.0	19.0	20.0	21.0
210	$F_3CCH_2I^+$	100	78.12	64.44	57.67	44.42	37.99	33.95	32.29	29.73	26.06
191	$F_2CCH_2I^+$	–	–	–	4.73	13.20	11.92	11.07	10.73	10.56	11.11
159	CHF_2I^+	–	–	–	–	–	–	0.63	0.70	0.86	1.10
146	IF^+	–	–	–	1.18	1.03	1.08	1.12	1.07	0.92	0.97
141	CH_2I^+	–	1.64	5.28	5.65	5.53	5.70	5.82	5.42	5.45	5.45
127	I^+	–	0.60	2.44	5.15	6.86	10.07	12.77	14.73	16.25	17.42
83	$F_3CCH_2^+$	–	15.46	20.59	16.15	12.91	11.00	10.21	9.75	9.36	8.87
82	F_3CCH^+	–	–	–	0.81	1.36	1.77	1.99	2.05	2.32	2.21
69	CF_3^+	–	–	–	–	–	0.42	0.46	1.11	1.59	1.97
64	$F_2CCH_2^+$	–	4.18	7.24	5.39	8.63	13.17	14.64	14.91	15.81	17.77
51	CHF_2^+	–	–	–	–	–	0.17	0.26	0.33	0.38	0.58
33	CH_2F^+	–	–	–	3.27	6.06	6.71	7.08	6.91	6.77	6.49

At photon energies above 14.3 eV we observe the formation of other fragment ions, although these channels present much lower relative intensities. The fragment IF^+ ($m/z=146$) which appears at approximately 14.38 eV, represent a recombination reaction involving the fragments of the C–I and C–F bond cleavages according to the pathways previously presented. This channel is very weak and yields less than 2% of the total ion yield in the VUV range. At about 14.63 eV we note the appearance of the fragment ion CH_2F^+ ($m/z=33$), also formed via recombination reaction. As previously discussed, this fragment may be formed from a complex multi-step reaction involving isomerization of the $CF_3CH_2^+$ fragment ion (reaction (1)) and subsequent dissociation of the C–C bonding. From the profile of the breakdown curve for the fragment ion with $m/z=83$, we clearly note an important decrease of the ion yield at energies above 14.3 eV. It indicates that this species is participating in additional competitive reactions, which may explain some of the recombination reactions observed. Starting from 14.88 eV we observe the fragment ion CF_3CH^+ ($m/z=82$). From 16.38 eV we see the appearance of the ion CF_3^+ ($m/z=69$) representing the rupture of the C–C bonding.

The lowest intensity ion fragments formed in the VUV photon energy range from the CF_2CH_2I molecule are CHF_2^+ ($m/z=51$) and CHF_2I^+ ($m/z=159$). These species first appear at approximately 16.63 eV and 17.38 eV, respectively, and their relative contribution are usually lower than 1%. Partial ion yields (PIY) for all cationic species generated from the photodissociation of trifluoroethyl iodide molecule are presented in Table 2, which represent the relative contribution of each ion to the PEPICO spectra at selected photon energies up to 21 eV.

These low intensity fragment ions are generated via complex multiple dissociation steps involving parallel and sequential reactions [4,36]. For a deeper analysis of the dissociation mechanisms for these complex reactions it would be required, for instance, the use of threshold electron techniques and RRKM statistical theory [4]. However, this treatment is beyond the scope of the present article.

The TOF mass spectrometer used in this work also allows measurements of PhotoElectron Photolon Coincidence (PEPICO) spectra. The PEPICO data [37] represent the time of flight of a pair of ions resulting from a dissociate photoionization event which are detected simultaneously. It relates the arrival of two correlated ions during a selected time window after the detection of an electron from the ionization process. In this sense, this technique is very useful to the study of the dissociation dynamics of multiply charged ions. However, in the energy range employed in the present article no multiply charged species have been observed, as expected, since the direct double ionization threshold is estimated to occur only at about 28 eV, based on a simple “rule of thumb” ($I^{++}/I^+ \approx 2.8$) [38]. Nevertheless, we have

recently performed experiments in the soft X-rays energy range for this molecule involving excitation and photodissociation from core edges, and recorded PEPICO, PEPICO and ion yield spectra. The results are under analysis and shall be presented in a forthcoming publication.

5. Summary and conclusions

We reported the photodissociation dynamics of the trifluoroethyl iodide molecule in gas phase following valence photoionization. TOF mass spectrometry, photoelectron photoion coincidence spectroscopy and synchrotron radiation have been employed. The PEPICO mass spectra have been recorded in the 10–22 eV range. From the analysis of the spectra as well as from our ab initio calculations we have been able to identify the photodissociation products and propose the dissociation mechanisms and determine appearance energies for the most intense fragmentation pathways for this molecule. Reliable electronic and molecular structure data were determined for the trifluoroethyl iodide molecule, its cation, and their fragment ions from our calculations using Moller–Plesset perturbation theory and density functional theory.

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